Hydrothermal Synthesis of $NaNb(BO_3)_2$ and $CaPb(BO_3)_2$, Analogues of Nordenskioldine - $CaSn(BO_3)_2$.

by
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Abstract

$NaNb(BO_3)_2$ and $CaPb(BO_3)_2$, analogues of nordenskioldine were synthesized in Mourey bombs at temperatures of 330 and 450 degrees C at pressures of 121.1 atmospheres and above. $NaNb(BO_3)_2$ forms colorless, tabular hexagonal crystals that are soluble in water and optically negative, $n_o \triangleq 1.52$, $n_e \triangleq 1.41$. $CaPb(BO_3)_2$ forms hexagonal prisms with perfect basal cleavage, $n_o = 1.707(5)$, $n_e = 1.601(3)$ with cell dimensions c= 13.38, a= 4.59 Angstroms. Further study of these products, the effect of substituting only for the Sn^{+4} ion in nordenskioldine, and of the system Na_2O-Nb_2O_5-B_2O_3-H_2O is required.

Introduction

Synthesis of various analogues of the mineral nordenskioldine has been accomplished by several authors (see Table 1). Schultze, et al, state "Appropriate attempts at preparation of LiNb, NaNb, and $KNb(BO_3)_2$ in agreement with investigations in the system Na_2O-Nb_2O_5-B_2O_3 (Burnett, Clinton, Miller, 1968) always yielded no boron bearing compounds."[1] However, except for Diman and Nekrasov[2] and Welty[3], who did hydrothermal work, all investigations were done with fluxed melts.

Nordenskioldine is isostructural with dolomite, and is found in Aro, Norway in an alkaline pegmatite with melanophanite, homilite, zircon, feldspar, molybdenite, cancrinite and analcite, and in an ore pipe in a marble near a granite contact at Arandis, South West Africa associated with tourmaline, cassiterite, calcite, siderite, stannite, chalcopyrite and pyrrhotite.[4] These parageneses suggest a high temperature hydrothermal origin. Therefore, it was decided to try and synthesize the NaNb analogue by hydrothermal means, and to duplicate Welty's CaPb analogue and continue research on it as he suggested.

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Table 1

Previously synthesized analogues of nordenskioldine

Authors	Analogues	Method
Diman and Nekrasov, 1965	CaSn MnSn FeSn BaSn MgSn	Hydrothermal
Vicat and Aleonard, 1966	MgSn MnSn SrSn CoSn CdSn BaSn NiSn CaSn	Fluxed Melts
Vicat and Aleonard, 1968	LuCr YCr YbCr DyCr ErCr	Fluxed Melts
Vicat and Aleonard, 1968	BaTi	Fluxed Melts
Schultze, Wilke, and Waligora, 1971	MgSn BaSn CoSn CaZr CaSn CdSn SrZr BaZr SrSn MnSn CdZr BaTi	Fluxed Melts
Welty, 1975	CaPb	Hydrothermal

Experimental Procedures

The procedures used in the syntheses are straightforward. Stoichiometric amounts of Nb_2O_5 and $Na_2B_4O_7$ in the synthesis of $NaNb(BO_3)_2$ or PbO_2 and $Ca(OH)_2$ in the case of $CaPb(BO_3)_2$ were loaded into either an iron "pot" bomb or a Mourey bomb with an excess of H_3BO_3 and the amount of double distilled demineralized water desired. The bomb was then sealed and placed into a furnace. After the desired time had elapsed, the bomb was removed and quenched in water. It was then opened and the contents examined.

This method has several attractive features. It is simple to perform and replicate, and involves no safety hazards. The pressure can be calculated directly from the percent fill and the temperature unless conditions are supercritical.

The reagents used are as follows:

Nb_2O_5	Ventron/Alfa Division, Lot No. 030779
$Na_2B_4O_7$	Mallinckrodt Chemical Works, Lot GMY
PbO_2	J.T. Baker Chemical Company, Lot No. 41703
$Ca(OH)_2$	J.T. Baker Chemical Company, Lot No. 43417
H_3BO_3	J.T. Baker Chemical Company, Lot No. 91188

The $Na_2B_4O_7$ was kept in the anhydrous state by heating it to well over 200 degrees C, the value given in the Handbook of Chemistry and Physics for driving off all water in borax ($Na_2B_4O_7 \cdot 10\ H_2O$) then stored in a desiccator until used.

All weighings were made on a Mettler electronic balance with an accuracy of $\pm$ 0.0002 grams. All samples were ground in a Fischer mortar grinder for a minimum of 15 minutes to insure homogeneity. Results of the runs are given in Table 2.

Table 2

Results of bomb runs

Time days)	Bomb/Seal Liner	Temp (C)	%Fill	Press (atm)	Reagents (g)	Products	Comments
14	Pot/Teflon Teflon	248 ± 5	100	37.9	Nb_2O_5; 2.6111 $Na_2B_4O_7$; 1.9821 H_3BO_3; 1.8077	Unreacted; Hexes prisms of $Na_2Nb_4O_{11}$	Mostly Nb_2O_5 left
38	Mourey/Ag Ag	450 ±5	100	*	Nb_2O_5; 2.6645 $Na_2B_4O_7$; 2.0138 H_3BO_3; 0.4531	Unreacted; $Na_2Nb_4O_{11}$; $NaNb(BO_3)_2$	Loss of seal occurred- only a small amount of water in chamber. Sides encrusted with hexagons of $NaNb(BO_3)_2$, bottom was $Na_2Nb_4O_{11}$
66	Pot/Teflon Teflon	248 ± 5	100	37.9	Nb_2O_5; 2.6432 $Na_2B_4O_7$; 1.9979 H_3BO_3; 1.5412	Unreacted; $Na_2Nb_4O_{11}$	Mostly $Na_2Nb_4O_{11}$, but same as run 1
35	Mourey/Ag Ag	330 ±5	100	127.1	PbO_2; 2.2342 $Ca(OH)_2$; 0.7407 H_3BO_3; 2.0310	Black prisms ($Ag_5Pb_2O_6$) Clear hexes, prisms, rhombs ($CaPb(BO_3)_2$) White needles, orange crystals	Nearly exact duplicatio of Welty's work
30	Pot/ Ag/ None	450 ±5	85	*	Nb_2O_5; 2.6582 $Na_2B_4O_7$; 2.0334 H_3BO_3; 1.2231	Unreacted; Black particles; $Na_2Nb_4O_{11}$	Loss of seal- no water present. Contents highly indurated.

Table 2, continued

Time (days)	Bomb/seal Liner	Temp (C)	%Fill	Press (atm)	Reagents (g)	Products	Comments
33	Mourey/Ag Ag	350 ±5	100	164.1	Nb_2O_5; 2.6554 $Na_2B_4O_7$; 2.0317 H_3BO_3; 1.2039	Unreacted; $Na_2Nb_4O_{11}$	Product is the same as that from runs 1,3,5.
10	Mourey/Ag Ag	400 ± 5	*	*	Nb_2O_5; 2.6618 $Na_2B_4O_7$; 2.0181 H_3BO_3; 0.5313	Unreacted; $Na_2Nb_4O_{11}$	Only a slight amount of water added to try and duplicate a leak.
78	Mourey/Ag Ag	450 ±5	100	*	Nb_2O_5; 2.6586 $Na_2B_4O_7$; 2.0337 H_3BO_3; 1.2154	Unreacted; $Na_2Nb_4O_{11}$; $NaNb(BO_3)_2$	$NaNb(BO_3)_2$ was well crystallized on sides of bomb in hexagons, trigonal and hexagonal prisms, and rhombohedrons. Pressure not directly calculable due to supercritical conditions.

Descriptions of Equipment Used

The iron "pot" bomb (figure 1) consists of a hollow steel cylinder with a flat plate on top that permits a steel cover to be bolted on very tightly. It can be used without a liner and with a silver seal covering the opening of the reaction chamber, or with a hollow Teflon cylinder inserted in it as a liner, and a Teflon seal. Use of the Teflon limits the maximum operating temperature to 250 degrees C. Otherwise, the bomb may be used up to 500 degrees C without danger of failure.

The Mourey bomb (figure 2) is a smaller, wider cylinder with a threaded top and bottom to provide greater seal strength. The reaction chamber is silver lined, and a silver seal is held on top of the chamber by a threaded plunger. This plunger is held down by the screw-on top and by a hex nut that fits on to the plunger.

The furnaces (figure 3) used were all base metal wound with windings connected in series with a Variac, an ammeter and a voltage regulator, so as to maintain a constant temperature. The temperature was measured by 400 and 500 degree C mercury thermometers. Rough calibration tables for the furnaces are given in Table 3.

Examinations

Examination of the products of the runs was undertaken by the following methods: Optical examination, using binocular and polarizing microscopes; Scanning electron microscopy; X-ray powder diffraction, using both diffractometer and powder camera; and

Figure 1

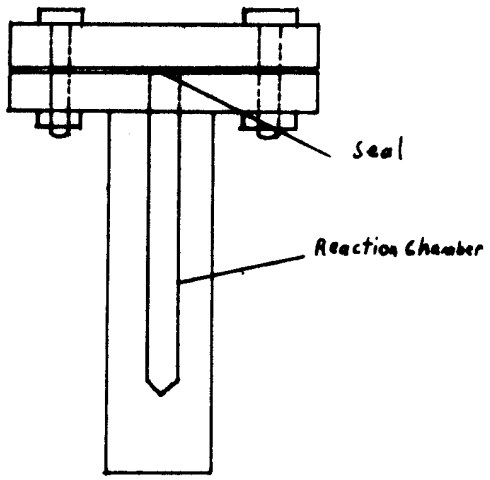


Figure 2

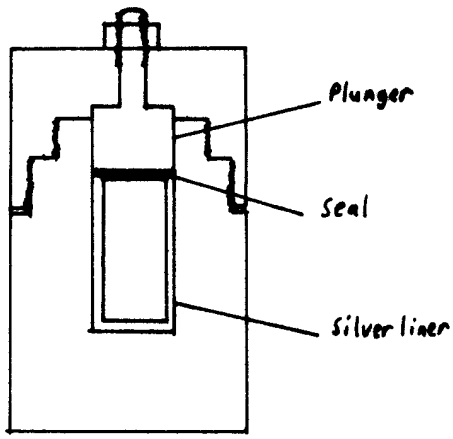


Figure 3

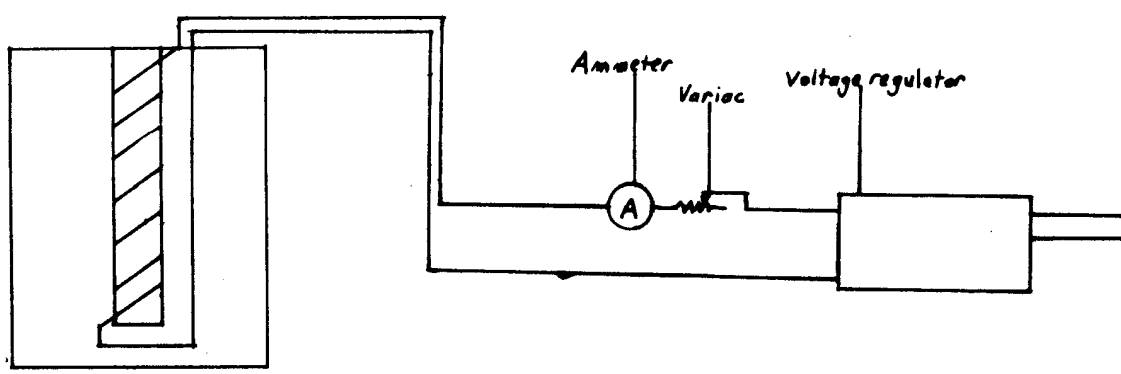


Table 3

Calibrations of Furnaces

Furnace 1

Amperes	Temperature (C)
0	22
1.0	112
1.1	132
1.2	158
1.3	177
1.4	199
1.5	220
1.6	246
1.7	269

Furnace 2

0	22
0.50	46
1.00	144
1.05	154
1.10	162
1.50	254
1.65	316
1.70	340
1.75	347
2.05	427
2.10	452
2.15	469

Furnace 3

0	21
1.00	110
1.50	200
1.75	256
1.85	284
1.90	297
2.00	324

single crystal x-ray diffraction, using a Weissenberg camera. The general procedure adhered to after opening of bomb and removal of contents was as follows: The material was studied under binocular and polarizing microscopes immediately following removal. Some material was heated in boiling double distilled demineralized water to remove soluble reactants and products, then reexamined with binocular and polarizing microscopes. X-ray and/or SEM study was then done if deemed necessary. The products studied in detail were $Na_2Nb_4O_{11}$ and those products believed to be $NaNb(BO_3)_2$ and $CaPb(BO_3)_2$.

$Na_2Nb_4O_{11}$ occurred as hexagon shaped crystals and prisms in all runs except run 4. The material was found at the bottom of the bombs and comprised the major part of the products in all runs except 1 and 7 where unreacted material exceeded it. Optical examination of the material showed that the index of refraction parallel to the long axis of the prisms was 1.542(5). The identity of the material in all runs was confirmed by comparison of diffraction patters with those of other runs and with the x-ray powder data file (see Table 4). Further information on this compound can be found in Andersson[5].

$NaNb(BO_3)_2$ occurred as hexagons with rhombohedral terminations in run 2, and as the same hexagons, plus trigonal and hexagonal prisms, and rhombohedrons in run 8. It was found lining the sides of the bombs in both cases. Examination under the binocular microscope showed the hexagons to be clear, the prisms tapering on either end, giving them a barrel shaped appearance. The prisms

Table 4

X-ray powder data

$Na_2Nb_4O_{11}$		Compound synthesized	
d A	I	d A	I
6.11	80	6.14	64
5.21	60		
5.14	80	5.15	25
4.66	40		
4.64	40	4.64	20
3.51	40	3.50	27
3.48	40		
3.06	100	3.06	100
3.02	100	3.02	88
2.988	80		
2.781	80	2.78	78
2.773	60		
2.751	80		
2.570	20	2.57	25
2.482	40	2.47	20
2.472	20		
2.459	40		

had a perfect basal cleavage and were very fragile. Under the polarizing microscope the hexagons gave a uniaxial negative figure that was off center about 15 degrees and showed a high birefringence, close to that of calcite. The indices of refraction were seen as $n_o \cong 1.52$, $n_e \cong 1.41$. Examination of the hexagons with the SEM proved them to have the same morphology as nordenskioldine (figure 4). The material is soluble in water and difficult to recrystallize afterwards. This, combined with the loss of some material in handling, left insufficient material for an x-ray study.

$CaPb(BO_3)_2$ occurred as hexagons with rhombohedral terminations, rhombohedrons, and hexagonal prisms in run 4. Studies of the other materials in this run can be found in Welty. All of the phases studied here contained inclusions of the other materials. The prisms had the same habit as those from the NaNb runs, and had the same basal cleavage. Cleavage plates of the prisms often had a zoned appearance, with the center of the zoning offset from the crystal center. Indices of refraction were measured as $n_o = 1.707(5)$, $n_e = 1.601(3)$. The hexagons and cleavage plates gave a 15 degree off center uniaxial negative figure, and the birefringence was less than that of the hexagons of the NaNb runs. Rotating crystal study of the material gave cell dimensions of $c = 13.38$, $a = 4.59$ Angstroms, and a zero layer Weissenberg picture showed no systematic omissions, which is consistent with the space group $R\bar{3}$, that of nordenskioldine. However, equipment failure prevented completion of x-ray characterization.

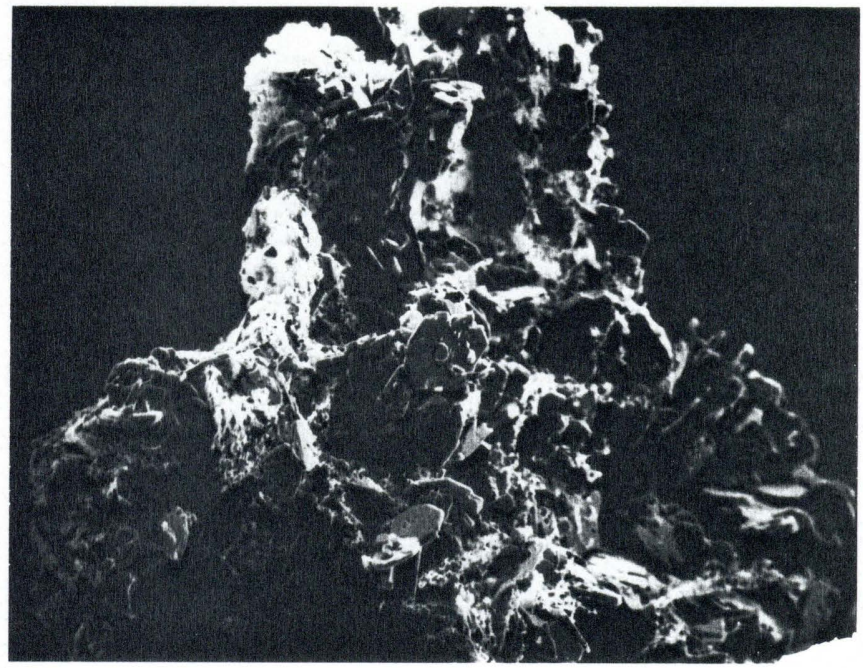
Discussion

From the morphological, optical, and x-ray data given here, and from the starting contents of the bombs, it is probable that the two substances are indeed $NaNb(BO_3)$ and $CaPb(BO_3)_2$. More work, however, needs to be done to establish this. Detailed optical analyses, single crystal x-ray studies, and chemical analyses can be performed to verify these conclusions.

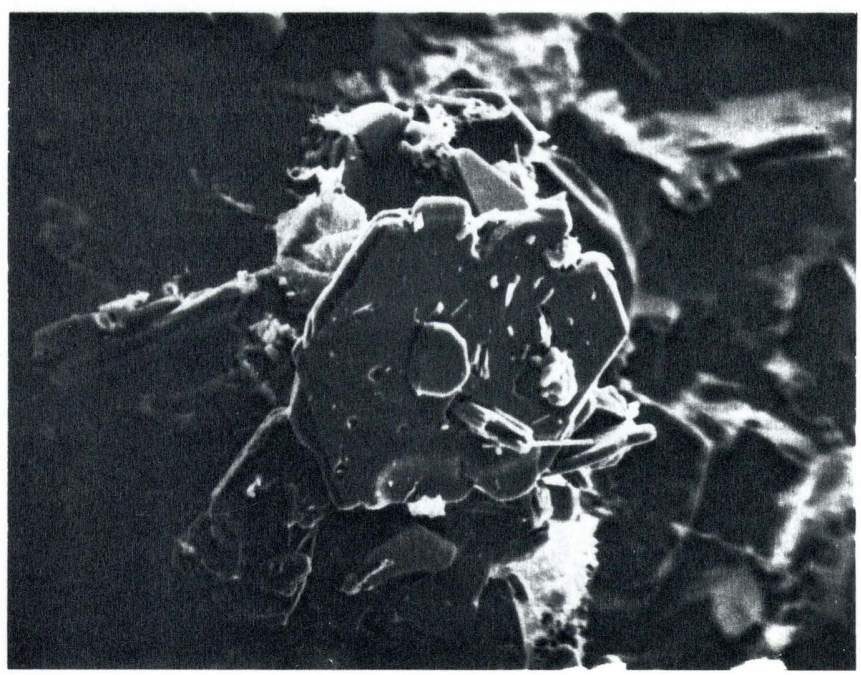
All of the published work on analogues of nordenskioldine has been either on substitution for the $^{+}2$ ion only, or for both ions. It would seem that there is a great deal of room for work on substitution solely for the $^{+}4$ ion similar to Vicat and Aleonard's[6] studies of the $^{+}2$ ion.

The NaNb analogue was only produced in the Mourey bombs with supercritical water. Their occurrence only on the sides of the bombs seems to indicate formation from a vapor. Below the critical point the only crystallized product was $Na_2Nb_4O_{11}$. In light of this, an in-depth study of the quaternary system Na_2O-Nb_2O_5-B_2O_3-H_2O would be in order to supplement the ternary system Na_2O-B_2O_3-Nb_2O_5 research by Burnett, Clinton and Miller[7].

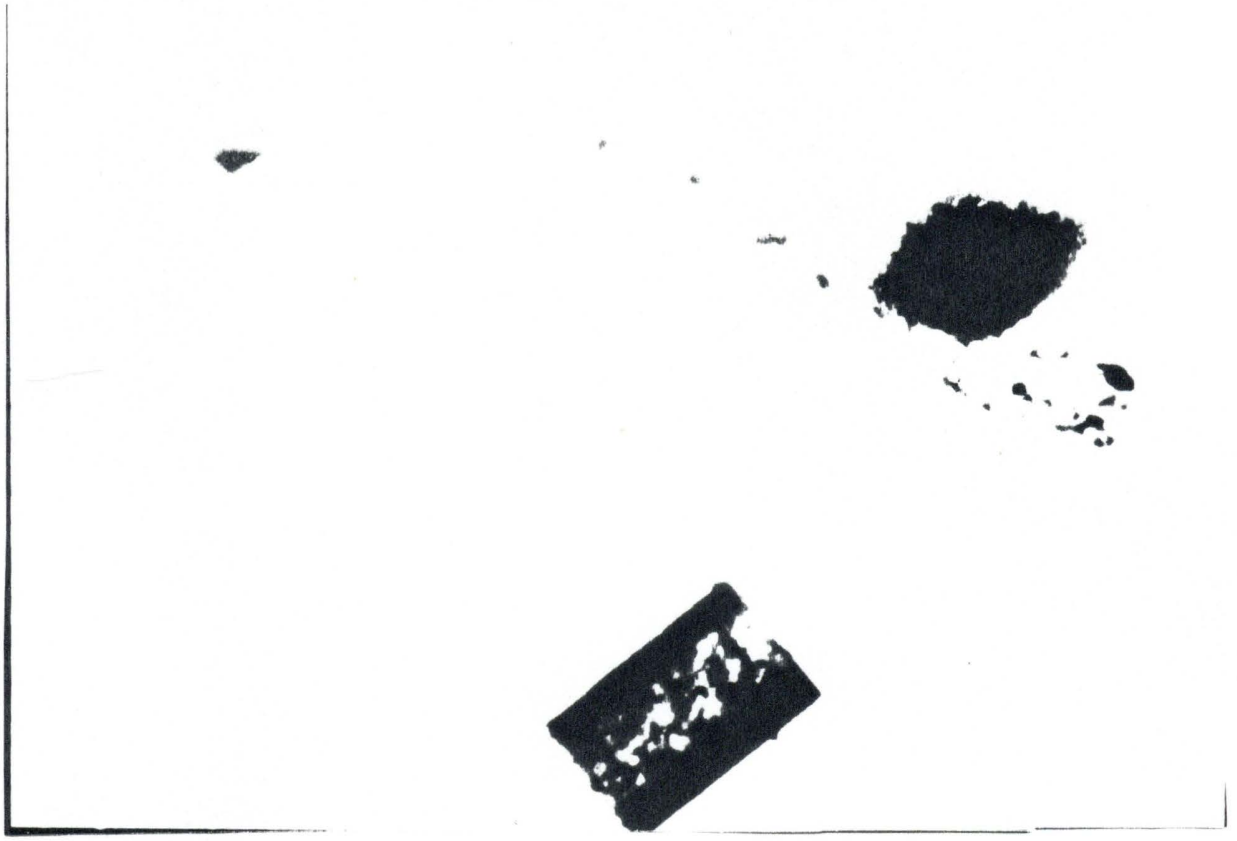
SEM micrographs of $NaNb(BO_3)_2$ from run 2- 500x



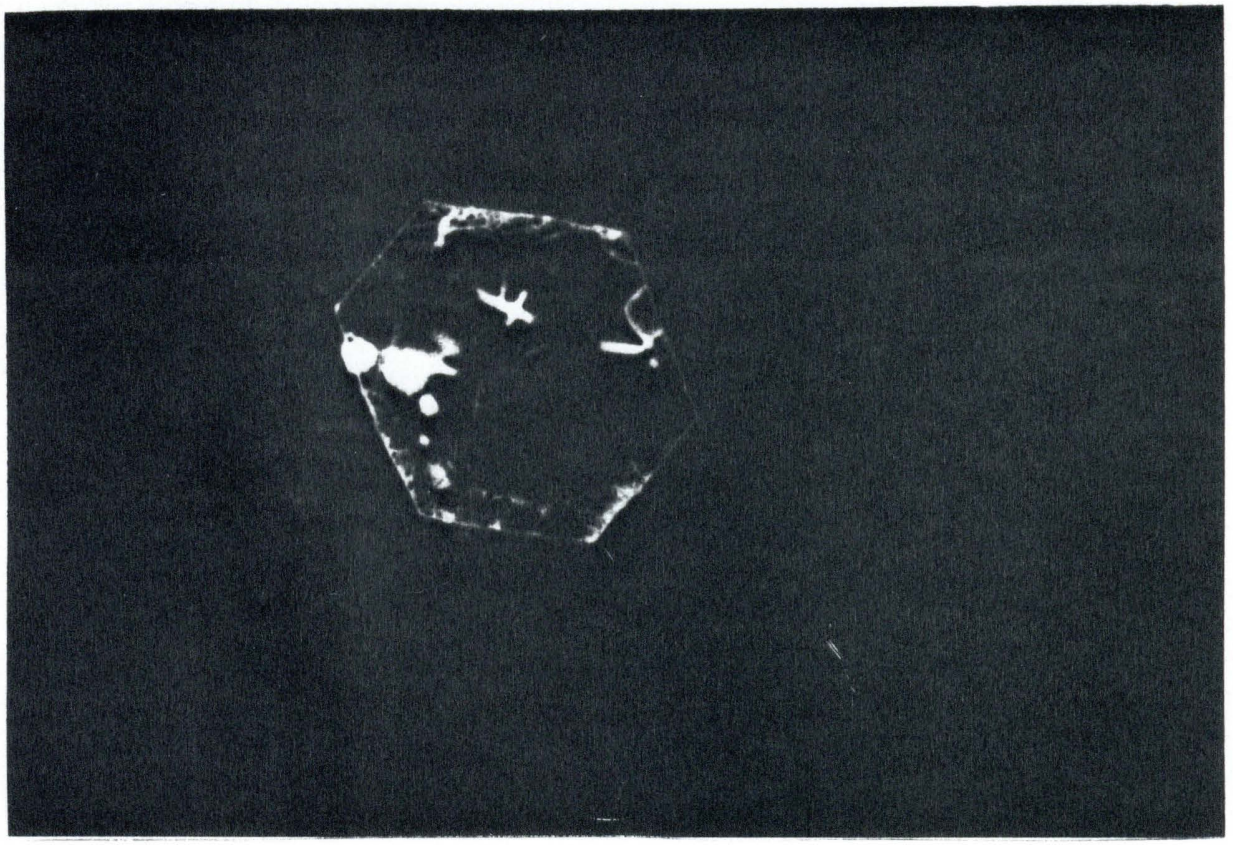
2000x



Polarizing microscope photographs of $CaPb(BO_3)_2$ from run 4
Rhombohedron and hexagonal prism- 20x



Cleavage plate from prism- 40x



References

1 Schultze, Von D., Wilke, K.Th., Waligora, C. (1971) Darstellung von Kristallinen Boraten M^{2+} M^{4+} $(BO_3)_2$. Zeit. Anorg. Chem. 380 37-40

2 Diman, Ye.N., Nekrasov, I.Ya., (1965) Hydrothermal Synthesis of Nordenskioldine and its Analogues. Doklady Akad. Nauk USSR 164 129-133

3 Welty, C.M. (1975) Hydrothermal Synthesis of $CaPb(BO_3)_2$, an Analogue of the Mineral Nordenskioldine. OSU Dept. of Geology & Mineralogy Senior Thesis, H.E. Wenden advisor

4 Palache, C., Berman, H., Frondel, C. (1951) Dana's System of Mineralogy 7th ed., Vol. 2, J.Wiley and Sons, New York 332-333

5 Andersson, S. (1967) Phase Analysis Studies on the $NaNbO_3$-Nb_2O_5, NaF-Nb_2C_5 and $NaNbO_3$-Nb_2O_5-H_2O Systems. Acta Chem. Scand. 21 1777-1782

6 Vicat, J., Aleonard, S. (1968) Etude' de Borates $MeMe'(BO_3)_2$ de Structure Dolomite. Mat. Res. Bull. 3 611-620

7 Burnett, D., Clinton, D., Miller, R.P. (1968) Some Phase Relationships Within the System Na_2O-B_2O_3-Nb_2O_5. Jour. Mat. Sci. 3 47-60

8 Aleonard, S., Vicat, J. (1966) Borates de Structure Dolomite. Bull. Soc. Franc. Mineral. Cryst. 89 271-272

10 Vicat, J., Aleonard, S. (1968) Borates de Terres Rares $TCr(BO_3)_2$ de Structure Dolomite. Bull. Soc. Franc. Mineral. Cryst. 91 293-295